

**The Henry constant for 20 hydrocarbons, CO₂ and H₂S in water as a
function of pressure and temperature¹**

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1 Paper presented at the Fourteenth symposium on Thermophysical Properties, June 25 – 30,
2000, Boulder, Colorado, USA

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ABSTRACT

The prediction of the solubility in water of hydrocarbon mixtures at high pressure and temperature is of crucial interest both for environmental reasons as for water-washing in hydrocarbon reservoirs.

A large number of experimental literature data has been analyzed using the Henry constant approach for the water phase, and a Peng-Robinson equation for the hydrocarbon phase. It has been shown that the Krichevsky-Kasarnovsky equation is applicable for describing the effect of pressure on the solubility[1]. The use of this equation requires the knowledge of the Henry's constant at the water vapor pressure and the partial molar volume at infinite dilution, for each hydrocarbon component. Taking Dhima's [2] expression for the partial molar volume, parameters for two correlation have been determined for the Henry constant as a function of temperature, for n-alkanes, cycloalkanes and for the major aromatic components.

KEY WORDS: Gases, Partial molar volume, Henry constants, Hydrocarbons, Solubility, Water

1. Introduction

As a result of the very low concentrations, the solubility of hydrocarbon components in water is difficult to measure. Nevertheless, it is well documented at ambient conditions, for environmental purposes. Under high pressure and high temperature conditions, however, a need has appeared to predict the hydrocarbon solubilities in order to better understand the compositional modification that may result from water-washing of hydrocarbon reservoirs (Lafargue & Le Thiez[3] ; de Hemptinne, et al. [4]).

The effect of pressure on the Henry's constant has been discussed by Dhima et al. [1]. The model, however, requires the Henry's constant as a function of temperature for each hydrocarbon component, at the water vapor pressure.

In this paper, we have looked at a large number of experimental data available in the literature and propose a Henry's constant model that is applicable from room temperature up to 200°C.

2. Modeling approach

The phase equilibrium calculation has been performed in the same manner as described by Dhima et al. [1] . The equilibrium is calculated using equality rule of the fugacities.

For the hydrocarbon phase, the fugacity is calculated using the Robinson & Peng [5] equation of state. The critical parameters used for this calculation are presented in table 1. The original

form of $a(T)$ is used for all components except for water. For this latter component, it was adapted so as to better reproduce its vapor pressure:

$$a = \frac{R^2 T_c^2}{P_c} \alpha_w(T_{r,w})$$

with

$$\alpha_w(T_{r,w}) = 1 + 1,81485214(1 - \sqrt{T_{r,w}}) + 0,32521776(1 - \sqrt{T_{r,w}})^2 \quad (1)$$

The conventional mixing rule has been used for the parameters a and b of the equation of state. The binary interaction parameters, k_{ij} , have been taken from various sources. They are summarized in table 2.

For the water phase, the fugacity is calculated using a different method for water and for the other components :

The fugacity of water in the aqueous phase is calculated using its vapor pressure :

$$f_w^{aq}(P, T, \bar{x}) \cong x_w^{aq} \cdot \phi_w^{sat}(P_w^{sat}, T) \cdot P_w^{sat} \cdot \exp\left[\frac{v_w^{l*}}{RT}(P - P_w^{sat})\right] \quad (2)$$

where the water activity coefficient in the aqueous phase is considered equal to unity.

The fugacity coefficient, $\phi_w^{sat}(P_w^{sat}, T)$, has been calculated using the expression given

by Li & Nghiem [6]. The saturated molar volume of the liquid water, v_w^{l*} , is

considered independent of pressure, and is calculated using the expression given by

Saul and Wagner [7]. The water vapor pressure, $P_w^{sat}(T)$, is also determined as

suggested by Saul and Wagner .

For the fugacity of the other components in the water phase, we use Henry's law approach, with the Krichevski-Kasarnovski correction for high pressure conditions:

$$f_i^{aq}(P, T, \bar{x}) = x_i^{aq} \cdot H_{i,w}^{\circ}(P_w^{sat}, T) \cdot \exp \frac{\bar{v}_i^{\infty}(T)(P - P_w^{sat})}{RT} \quad (3)$$

where it is assumed that the activity coefficient related to the Henry constant is one, as was shown in [1].

The partial molar volume at infinite dilution, $\bar{v}_i^{\infty}(T)$, is calculated as suggested by Dhima [2], using an improvement of the Lyckman et al. [8] equation :

$$\bar{v}_i^{\infty}(T) = \left[\bar{v}_i^{\infty}(T) \right]_{Lyckman} + \left(\frac{dv_w}{dT} \right)^{sat} (T - 298,15) \quad (4)$$

where $\left(\frac{dv_w}{dT} \right)^{sat}$ is the derivative of the volume of water at its vapor pressure with temperature.

Using experimental data, we have determined the Henry's constant, $H_{i,w}^{\circ}(P_w^{sat}, T)$, by using the criterion of equal fugacity :

$$\ln(H_{i,w}^{\circ}(P_w^{sat}, T)) = \ln \left(\frac{f_i^{HC}}{x_i^{aq}_{exp}} \right) - \frac{\bar{v}_i^{\infty}(T)(P - P_w^{sat})}{RT} \quad (5)$$

This expression is used for H₂S, CO₂ and 20 hydrocarbon species that might occur in hydrocarbon reservoirs.

Two different expressions are tested in this paper for describing the Henry constant as a function of temperature. The major improvement compared to previous equations is the fact that the number of parameters is reduced to a minimum of 3, and that the same expression is used for all components, both gases and liquids. The first expression is a simple polynomial of the inverse of temperature:

$$\ln(H_{i,w}^{\circ}(T)) = A_i + \frac{B_i}{T} + \frac{C_i}{T^2} \quad (6)$$

The choice of the second equation was motivated by a recent paper of Tsonopoulos [9] who indicated that the heat of solution of hydrocarbons in water is a linear function of temperature. The logical consequence on the Henry's constant is that the third term should show a logarithm of temperature:

$$\ln(H_{i,w}^{\circ}(T)) = A'_i + \frac{B'_i}{T} + C'_i \ln(T) \quad (7)$$

The parameters for these equations have been determined by minimizing the objective function:

$$OF = \sum_k \left(\frac{(H_{i,w}^{\circ}(T))^{\text{exp}} - (H_{i,w}^{\circ}(T))^{\text{cal}}}{(H_{i,w}^{\circ}(T))^{\text{exp}}} \right)^2 \quad (8)$$

3. Data base

The data base used for fitting the parameters of equations (6) and (7) was smaller than that used for a statistical evaluation of the results.

For the parameter fitting, we have based ourselves on the database already presented by Dhima et al. [1]. It has been completed for a number of components, which have not been looked at by Dhima et al. The references are given in table 3. Most of the data, that are not specifically referred to, come from the Dortmund Data Bank [10]. A selection of the available data is made so as to be more representative of the full temperature and pressure range that is aimed at (20 to 200°C and pressures up to 1000 bar). In addition, for the heavier components where the data are very scattered, a selection was made so as to retain only the data that were coherent among different authors.

In a second stage, all data available in the Dortmund Data Bank have been used for a statistical evaluation of the calculated solubility. The VLE, LLE and Gas solubility bases have been brought together for this purpose. Only very few data have been removed. As a result, large statistical deviations may mean either that the model and its parameters is not adapted, but more likely it reflects the large scatter in experimental data. For example, the octane – water solubility data are shown on figure 1. At 25°C, solubility data (in ppm molar) range from 0.068 to 0.14, a difference of 100%.

4. Results

The parameters that have been obtained using the above regression method are presented in tables 4 and 5.

A statistical evaluation of the results is shown in table 6. The standard deviation is generally a good estimate of the ability of the model to reproduce experimental data. It is defined here as:

$$\text{StandardDeviation} = \sqrt{\frac{1}{N-1} \sum_k \left(\frac{(x_i)^{\text{exp}} - (x_i)^{\text{cal}}}{(x_i)^{\text{exp}}} \right)^2} \quad (9)$$

The bias is also provided in order to indicate whether the model tends to overpredict or underpredict the data. It is calculated from:

$$\text{Bias} = \frac{\sum_k \left(\frac{(x_i)^{\text{exp}} - (x_i)^{\text{cal}}}{(x_i)^{\text{exp}}} \right)}{N} \quad (10)$$

Some general trends can be pointed out

- The standard deviation is noticeably larger for heavier components, reflecting the larger scatter in experimental data.
- Figure 2 illustrates how the Henry's constant equation (6) shows a much larger curvature than equation (7). The truth appears to lie somewhere in-between. In view of the scatter of the experimental data, it did not seem worthwhile to try a four-parameter equation that would take both the square of the reciprocal temperature and the logarithm of the temperature.
- As a result of this different behavior, equation (6) very clearly indicates a minimum solubility, while equation (7) does not show this trend. The difference is clearly shown in figure 3, showing the solubility of n-heptane with temperature. The scatter in the experimental data is too large to tell which form is the better one.

One of the objectives of this work was to evaluate whether a generalized behavior of the Henry constant could be observed within a given chemical family. Figures 4 and 5 have been plotted for that purpose, but no definitive response good be given.

- The Henry constant of the normal alkanes as a function of temperature is plotted in Figure 4. It appears that they are essentially parallel, and decrease from nonane to methane. The

values of methane and ethane are almost similar. The behavior of the n-decane Henry constant is unlike the others. The results for this component must be taken with caution, however, since the experimental data are very scattered.

If we remove methane, whose behavior at low temperature is a bit different, and decane, one could write the Henry constant as:

$$\ln(H_{i,w}^{\circ}(T)) = \ln(H_{ethane,w}^{\circ}(T)) + 0.0306n^2 + 0.712n - 0.272 \quad (11)$$

where n indicates the carbon number. This expression has not been further evaluated, and is probably only valid within a limited temperature range.

- Figure 5 shows the same plot for aromatics. Again, it appears that the heavier component have larger Henry constants, but the behavior is no longer parallel. All aromatics seem to show a similar value close to room temperature. The xylenes have identical values.

5. Comparison with other Henry's constant expressions

Several other papers have proposed expressions for Henry's constants as a function of temperature. They are summarized in table 7. The functional form is often similar or identical to the one proposed here. However, none of the proposed expressions have been fitted on as many components and as many data points as has been done in this work. As a result, the standard deviation that is observed between the experimental and the calculated Henry's constants is usually slightly larger (table 8). The standard deviation that is calculated here is based on the Henry constant, rather than on the solubility:

$$\text{StandardDeviation} = \sqrt{\frac{1}{N-1} \sum_k \left(\frac{(H_{i,w}^\circ(T))^{\text{exp}} - (H_{i,w}^\circ(T))^{\text{cal}}}{(H_{i,w}^\circ(T))^{\text{exp}}} \right)^2} \quad (12)$$

The large difference in magnitude between the different methods is essentially due to the scatter in experimental data, which may not be the same for one compound or the other.

Hence, it is difficult to comment on the differences between different components.

For a given component, some literature methods appear to be much worse than the ones proposed here. The most obvious reason for that is that the Henry constant is not truly an experimental value. As seen in equation (5), its value depends also on the way the fugacity is calculated. Tsonopoulos & Wilson [14], for instance, use the vapor pressure with a Poynting correction, but don't take into account the presence of water in the hydrocarbon phase, that may become important at higher temperature. We have used a Peng-Robinson method, as it is the method that is most commonly used in petroleum engineering. The choice of a conventional mixing rule for the parameter a , with the k_{ij} parameters shown in table 2, probably also has an effect. Hence, our results are strictly speaking only valid for the above described model.

For ethylbenzene, the much better results of the Heidman et al. [15] expression is easily understood when considering figure 6. It shows, as was indicated earlier, that the experimental data fall between the two proposed expressions at low temperature. The four-parameter equation that is proposed by Heidman et al. [15] fits this domain much better. However, at higher temperature, it over-estimates the Henry constant. Since most data points are located below 100°C (373 K), the average deviation will consider this low temperature domain with a much larger weight than the high temperature range, which is the domain that we want to focus on.

6. Conclusions

We have proposed two three-parameter correlations for the calculation of the Henry constant of major petroleum fluids components in water. The first correlation is quadratic with the reciprocal temperature, the second uses the logarithm of the temperature. Both of these correlations have been fitted to a large number of experimental data, essentially coming from the Dortmund Data Bank.

The average deviation on the solubility data indicates essentially the scatter in the data used, which varies from one component to another. The acquisition of additional data is of crucial importance for improving the large uncertainties, especially for heavy components at high temperatures.

The evolution of the Henry constant with carbon number has been visualized for n-alkanes and aromatics. A possible generalization method has been proposed for n-alkanes.

The two correlations have been compared to some other correlations that have already been proposed in the literature. Their performance is of the same order, compared to the experimental Henry constants. The major contribution of this paper is however to offer expressions that are applicable to a large number of components.

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Table 1 : Critical properties used for the model calculations

	Tc (K)	Pc(Pa)	ω
water	647.3	2.21E+07	0.344
H2S	373.2	8.94E+06	0.081
Methane	190.4	4.60E+06	0.011
CO2	304.2	7.38E+06	0.239
Ethane	305.4	4.88E+06	0.099
Propane	369.8	4.25E+06	0.153
n-Butane	425.2	3.80E+06	0.199
i-Butane	408.2	3.65E+06	0.183
n-Pentane	469.7	3.37E+06	0.251
i-Pentane	456.4	3.39E+06	0.227
cyclopentane	511.7	4.51E+06	0.196
cyclohexane	553.5	4.07E+06	0.212
Methylcyclohexane	572.2	3.47E+06	0.236
Benzene	562.2	4.89E+06	0.212
n-Hexane	507.5	3.01E+06	0.299
n-Heptane	540.3	2.74E+06	0.349
Toluene	591.8	4.10E+06	0.263
n-Octane	568.8	2.49E+06	0.398
Ethylcyclohexane	610.5	3.18E+06	0.293
Ethylbenzene	617.2	3.60E+06	0.302
o-Xylene	630.3	3.73E+06	0.310
p-Xylene	616.2	3.51E+06	0.320
m-Xylene	617.1	3.54E+06	0.325
n-Nonane	594.6	2.29E+06	0.445
n-Decane	617.7	2.12E+06	0.489

Table 2 : Binary interaction parameter between water and the component indicated

	k_{ij}	ref
CO ₂	0.1896	[10]
H ₂ S	0.13	[10]*
Methane	0.5	[11]
Ethane	0.5	[11]
Propane	0.52	[11]
n-Butane	0.54	[11]
i-Butane	0.5	[12]
n-Pentane	0.5	[12]
i-Pentane	0.5	[12]
n-Hexane	0.496	[12]
Cyclohexane	0.5	[12]
Benzene	0.28	[12]
n-Heptane	0.4583	[12]
Methylcyclohexane	0.5	[12]
Toluene	0.285	[12]
n-Octane	0.456	[12]
Ethylbenzene	0.3	[12]
o-Xylene	0.3	[12]
p-Xylene	0.3	[12]
m-Xylene	0.3	[12]
n-Nonane	0.455	[12]
n-Decane	0.454	[12]

* According to [10] k_{ij} is a function of temperature for H₂S. We have used a fixed value, taken at 100°C.

Table 3: Data used for parameter fitting

Hydrocarbon component	N pts	T range (K)	P range (MPa)	Ref
H2S	39	303-443	1.7-2.34	Burgess & German (1969)
	10	313-378	2.8-9.24	Carroll & Mather (1989)
	25	311-478	0.3-7.5	Gillespie & Wilson (1980)
	32	310-477	4.1-20.7	Gillespie & Wilson (1982)
	324	283-453	0.2-6.7	Lee & Mather (1977)
CO2	42	285-313	2.53-50.66	Wiebe, R. & V.L. Gaddy (1940)
	27	323-373	2.53-70.93	Wiebe, R. & V.L. Gaddy (1939)
	25	374-393	2.33-70.32	Prutton & Savage : (1945)
	32	323-473	20-350	Tödheide & Franck : (1963)
	87	383-543	10-150	Takenouchi & Kennedy (1964)
	29	289-394	0.69-20.28	Gillespie & Wilson (1982)
	43	373-473	0.33-8.11	Müller et al. (1988)
	4	323-348	10-15	D'Souza et al. (1988)
	28	353-471	2.11-10.21	Nighswander et al. (1989)
	7	348-421	10-20	Sako et al. (1991)
	26	288-298	6.08-24.32	King et al. (1992)
	3	323	10.1-30.1	Dohrn et al. (1993)
	41	313-333	0.06-1.57	Fischer et al. (1995)
	10	278-338	0.049-0.084	Zheng et al. (1997)
	7	344	10-100	Dhima et al. (1999)
Methane	6	323	5-21	Michels et al. (1936)
	72	298 - 444	2 - 68	Culberson & McKetta (1951)
	7	298	2 - 5	Duffy et al. (1961)
	18	325 - 398	10 - 61	O'Sullivan & Smith (1970)
	8	311 - 344	4 - 34	Amirijafari & Campbell (1972)
	32	423 - 523	5 - 108	Sultanov et al. (1972a)
	12	473 - 523	9 - 98	Sultanov et al. (1972b)
	29	423 - 523	20 - 250	Sanchez (1978)
	17	427-479	3-192	Price (1979)
	6	423-478	1-14	Gillespie & Wilson (1982)
	15	298-338	3-12	Yarym-Agaev et al. (1985)
	6	283-298	1-5	Wang et al. (1995)
	8	283-343	0.18-0.26	Reichl (1996)
	17	274-286	1-9	Lekvam & Bishnoi (1997)
	7	324	10-58	Gao et al. (1997)
	4	344	20-100	Dhima et al. (1998)
Ethane	58	311-444	2-68	Culberson & McKetta (1950)
	32	473-573	20-350	Danneil et al. (1967)
	3	344	3-27	Anthony & McKetta (1967)
	4	344	20-100	Dhima et al. (1998)

Table 3, continued : Data used for parameter fitting

Hydrocarbon component	N pts	T range (K)	P range (MPa)	Ref
Propane	43	285-422	1-19	Kobayashi & Katz (1953)
	4	273	0.03-0.1	Umano et al. (1958)
	8	344	0.51-1.25	Wehe & McKetta (1961)
	68	289-411	0.1-3.44	Azarnoosh & McKetta (1958)
n-Butane	15	311-378	7-69	Brooks et al. (1951)
	101	311-478	1-69	Reamer et al. (1952)
	114	311-511	1-69	Sage & Lacey (1955)
	19	298-423	0.1-4.13	Caroll et al. (1997)
	5	344	10-100	Dhima et al. (1998)
	94	276-410	0.1 – 3.38	All DDB GLE data
n-Pentane	34	310-588.71	0.62-20.69	Gillespie & Wilson (1982)
	7	298-422	3Ph	Price (1976)
n-Hexane	9	313-422	3Ph	Tsonopoulos & Wilson (1983)
	5	373-463	3Ph	Barrufet et al. (1996)
	10	298-425	3Ph	Price (1976)
n-Heptane	2	310-394	3Ph-13.79	Ng & Chen (1995)
	7	298-423	3Ph	Price (1976)
n-Octane	6	311-539	3Ph	Heidman et al. (1985)
	7	298-422	3Ph	Price (1976)
	11	310-552	3Ph	Brady et al. (1982)
n-Nonane	5	298-409	3Ph	Price (1976)
n-Decane	4	310-394	3Ph-13.79	Ng & Chen (1995)
cyclohexane	1	298.15	0.1	Mc Auliffe (1963)
	1	298	0.1	Leinonen & McKay (1973)
	5	278-318	3Ph	Pierroti (1972)
	1	298	0.1	Mc Auliffe (1966)
	6	329-494	3Ph	Guseva (1963)
	6	313-482	3Ph	Tsonopoulos & Wilson (1983)
methylcyclohexane	9	298-423	3ph	Price (1976)
Benzene	163	273-478	0.1-34.47	All DDB LLE data
Toluene	52	289-473	0.1-2.3	DDB LLE data
o-xylene	6	273-298	0.1	DDB LLE data
	5	273-318	3Ph	Solubility Data Series
m-xylene	19	221-473	3ph	DDB LLE data
p-xylène	11	273-363	3Ph	Solubility Data Series
	19	298-461	3Ph	DDB LLE data
Ethylbenzene	6	311-553	3Ph	Brady et al. (1982)
	7	311-568	3Ph	Heidman et al. (1985)
i-butane	3	278-318	0.1	Wetlaufer et al. (1964)
	4	283-313	0.2-0.5	Kazarayan & Ryabtsev (1969)
	1	298	0.1	McAuliffe (1966)
	1	298	0.1	Rudakov (1979)
i-pentane	1	298	0.1	McAuliffe (1966)
	1	298	0.1	McAuliffe (1963)
	2	273-298	0.1	Polak (1973)

Table 4 : Parameters used for equation 6 (Dhima)

Component	A	B	C
H ₂ S	-2.25054E+00	5.98511E+03	-1.23934E+06
CO ₂	-6.02700E-01	5.85739E+03	-1.23934E+06
Methane	-2.17210E+00	7.88560E+03	-1.41960E+06
Ethane	-5.05560E+00	1.02260E+04	-1.88690E+06
Propane	-4.72710E+00	1.03790E+04	-1.94660E+06
n-Butane	-4.79700E+00	1.05020E+04	-1.97330E+06
n-Pentane	-1.39440E+01	1.75250E+04	-3.21048E+06
n-Hexane	-2.12050E+01	2.27800E+04	-4.09730E+06
n-Heptane	-2.07040E+01	2.32560E+04	-4.24550E+06
n-Octane	-1.78779E+01	2.11689E+04	-3.84600E+06
n-Nonane	-1.15522E+01	1.73764E+04	-3.20999E+06
n-Decane	-8.49938E+00	1.51461E+04	-3.21001E+06
Cyclohexane	-1.57846E+01	1.74832E+04	-3.21000E+06
Methylcyclohexane	-1.40357E+01	1.72513E+04	-3.21000E+06
Benzene	-7.25950E+00	9.85280E+03	-1.98960E+06
Toluene	-1.54989E+01	1.64168E+04	-3.21000E+06
o-Xylene	-1.51752E+01	1.63935E+04	-3.21000E+06
m-Xylene	-1.51752E+01	1.63935E+04	-3.21000E+06
p-Xylene	-1.51142E+01	1.63908E+04	-3.21000E+06
EthylBenzene	-1.30204E+01	1.57165E+04	-3.21001E+06
IsoButane	-4.26505E+00	1.03790E+04	-1.94660E+06
IsoPentane	-1.89708E+01	1.90952E+04	-3.20998E+06

Table 5: Parameters used for equation 7 (Tsonopoulos)

Component	A	B	C
H ₂ S	2.18415E+02	-1.19995E+04	-3.06136E+01
CO ₂	2.16324E+02	-1.19995E+04	-3.00261E+01
Methane	2.37150E+02	-1.19990E+04	-3.31160E+01
Ethane	2.01791E+02	-1.05000E+04	-2.78321E+01
Propane	2.44299E+02	-1.26500E+04	-3.39873E+01
n-Butane	2.10245E+02	-1.10007E+04	-2.89762E+01
n-Pentane	2.19285E+02	-1.10006E+04	-3.04489E+01
n-Hexane	4.24975E+02	-2.18500E+04	-6.01168E+01
n-Heptane	3.37548E+02	-1.75000E+04	-4.72333E+01
n-Octane	4.16580E+02	-2.17000E+04	-5.86225E+01
n-Nonane	4.16580E+02	-2.17000E+04	-5.86225E+01
n-Decane	1.91119E+02	-1.20001E+04	-2.53513E+01
Cyclohexane	2.20507E+02	-1.19995E+04	-3.04633E+01
Methylcyclohexane	2.22981E+02	-1.19994E+04	-3.06977E+01
Benzene	2.10645E+02	-1.19891E+04	-2.93200E+01
Toluene	2.06190E+02	-1.20000E+04	-2.85130E+01
o-Xylene	2.00990E+02	-1.19999E+04	-2.76004E+01
m-Xylene	2.00990E+02	-1.19999E+04	-2.76004E+01
p-Xylene	2.02296E+02	-1.19999E+04	-2.78197E+01
EthylBenzene	2.03930E+02	-1.19998E+04	-2.80236E+01
IsoButane	2.44710E+02	-1.26500E+04	-3.39873E+01
IsoPentane	2.42283E+02	-1.19991E+04	-3.38838E+01

Table 6: Deviations observed with the two different expressions for Henry's constants

Component	Nb of points	Standard deviation (%) Equation 6 (Dhima)	Bias (%)	Standard deviation (%) Equation 7 (Ts)	Bias (%)
H2S	963	14.7	4.5	25.3	9.7
CO2	1125	17.5	-0.8	23.7	3.8
Methane	702	17.2	-1.7	20.4	2.72
Ethane	366	18.7	-2.1	18.8	-3.6
Propane	187	11.1	2.7	10.6	0.4
n-Butane	342	30.7	12.2	31.6	12.8
n-Pentane	38	22.4	-9.9	30.6	2.0
n-Hexane	29	34.0	-7.3	33.4	-12.4
n-Heptane	19	37.7	-2.0	30.4	-13.8
n-Octane	23	54.9	4.4	54.8	8.1
n-Nonane	5	51.9	11.7	60.3	-5.8
n-Decane	5	105.9	39.9	80.0	28.2
Cyclohexane	17	30.4	6.2	24.7	3.7
Methylcyclohexane	11	33.3	-6.4	39.5	-3.9
Benzene	163	22.1	4.4	22.3	5.3
Toluene	53	28.3	10.1	25.4	4.4
o-Xylene	11	23.3	-16.9	7.5	0.0
m-Xylene	20	21.2	-0.1	16.4	3.8
p-Xylene	30	18.3	-10.9	19.1	18.0
EthylBenzene	39	37.3	21.5	19.9	-10.4
IsoButane	9	8.2	1.1	9.6	1.5
IsoPentane	4	14.0	3.3	23.0	9.7

Table 7 : Other Henry constant models available in the literature

Henry's constant expression	Solute investigated
$\ln H^* = \ln f_w^{\text{sat}} + A + B/T + C/T^2$	Methane, Ethane, Propane, Propane, Butane, Pentane, Octane, CO ₂ .
$\ln H = A + B/T + CT^2 + D \ln T$	Benzène, Cyclohexane, Hexane.
$\ln H = A + B/T + CT^2 + D \ln T$	Ethylcyclohexane, Octane, Ethylbenzene.
$\ln H = A + B/T + C/T^2 + D/T^3$	Methane, Ethane
$\ln H = A + B/T + C/T^2$	CO ₂ for T < 353 K
$\ln H = A(1-T^*)^{1/3}/T + B + C/T + D/T^2$	CO ₂ for T > 353 K
$\ln H = \ln P_w^{\text{sat}} + A/T^* + B(1-T^*)^{0.355}/T^* + \exp(1-T^*)(T^*)^{-0.41}$	Methane, Ethane, CO ₂ , H ₂ S + Gaz.
$\ln H = A + B/T + C/T^2 + D/T^3$	Methane, Ethane.
$\ln H = A + BT + C/T + D \ln T$	Propane
$\ln H = A + BT + C/T + D \ln T$	Butane

T* indicates the reduced temperature of water : T*=T/647.14

P_w^{sat} is the water vapour pressure

f_w^{sat} is the water fugacity at saturation

Table 8: Comparison of the standard deviation (in %) for the determination of the Henry constant, for different literature methods, and the equations (6) and (7)

	Methane	Ethane	Propane	Butane	Pentane	Benzène	Cyclohexane	Hexan
Number of experimental points	702	359	187	342	38	163	18	26
Tsonopoulos & Wilson (1983)						42.	56.	39.
Heidman et al. (1985)								
Li & Nghiem (1986)	36.	18.	8.7	24.	63.			
Prini & Crovetto (1989)	42.	19.						
Crovetto (1991)								
Harvey (1996)	45.	19.						
Carroll & Mather (1997)	44.	*	9.7					
Carroll et al. (1997)				22.				
$\ln(H^\circ)=A+B/T+C/T^2$ (eq. 6)	41.	19.	9.1	22.	35.	20.	32.	37.
$\ln(H^\circ) = A+B/T +C*\ln(T)$ (eq. 7)	35.	21.	8.8	19.	33.	16.	24.	40.

* a typing error must have occurred in the paper of Carroll & Mather [19] since the calculated values have no sense.

Figure 1: n-Octane solubility in water as a function of temperature

Figure 2: Comparison of the behavior of Henry's constant for the equations 6 and 7. The example shown is for n-Pentane.

Figure 3: n-Heptane solubility in water as a function of temperature, compared with the values calculated using equations (6) and (7)

Figure 4: Evolution of the Henry constant for n-alkanes, calculated with expression (6)

Figure 5: Evolution of the Henry constant for aromatics, calculated with expression (6)

Figure 6 : The Henry constant for Ethylbenzene, as calculated using equation (6), equation (7) and as calculated by the equation of Heidman [15]

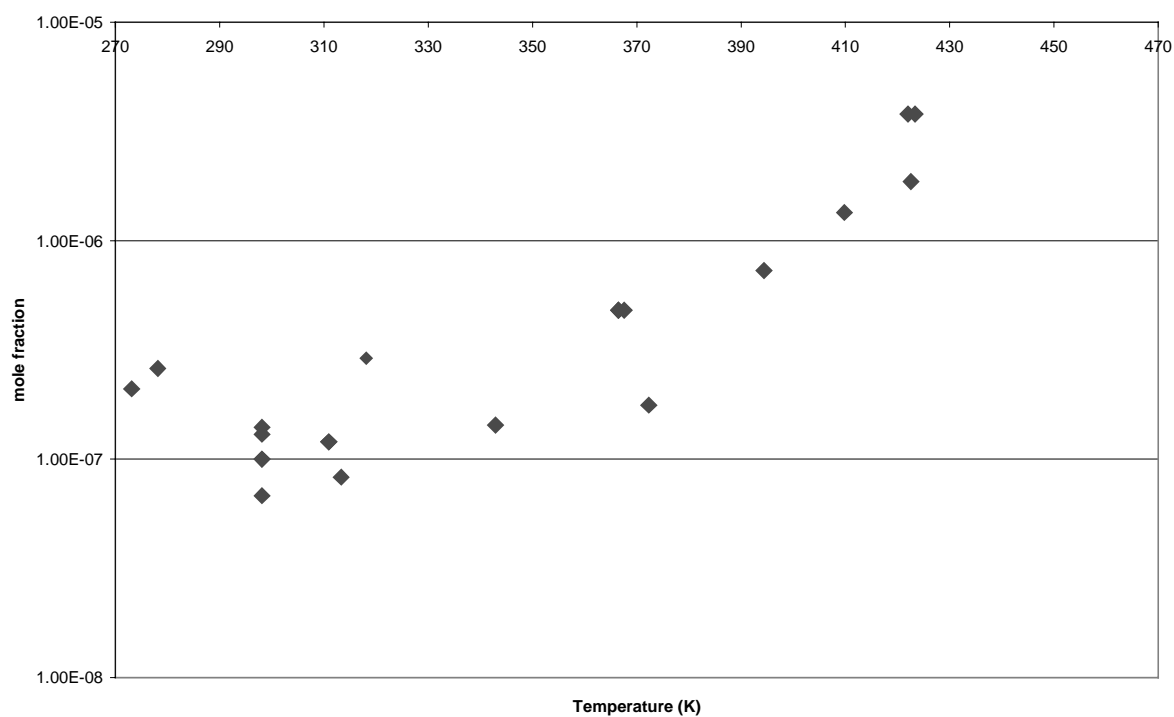


Figure 1: n-Octane solubility in water as a function of temperature

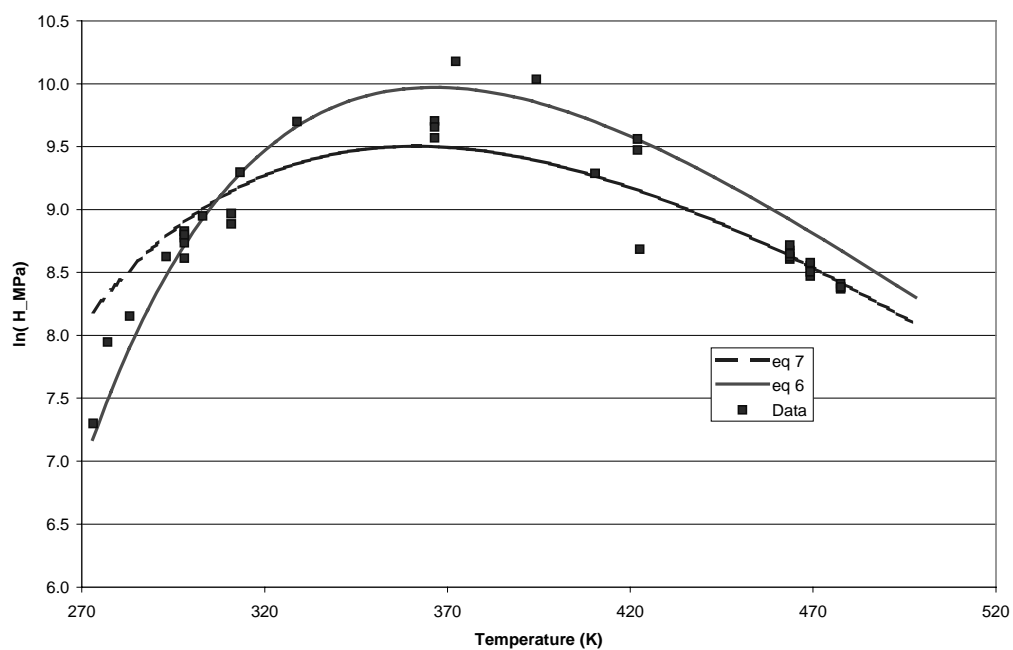


Figure 2: Comparison of the behavior of Henry's constant for the equations 6 and 7. The example shown is for n-Pentane.

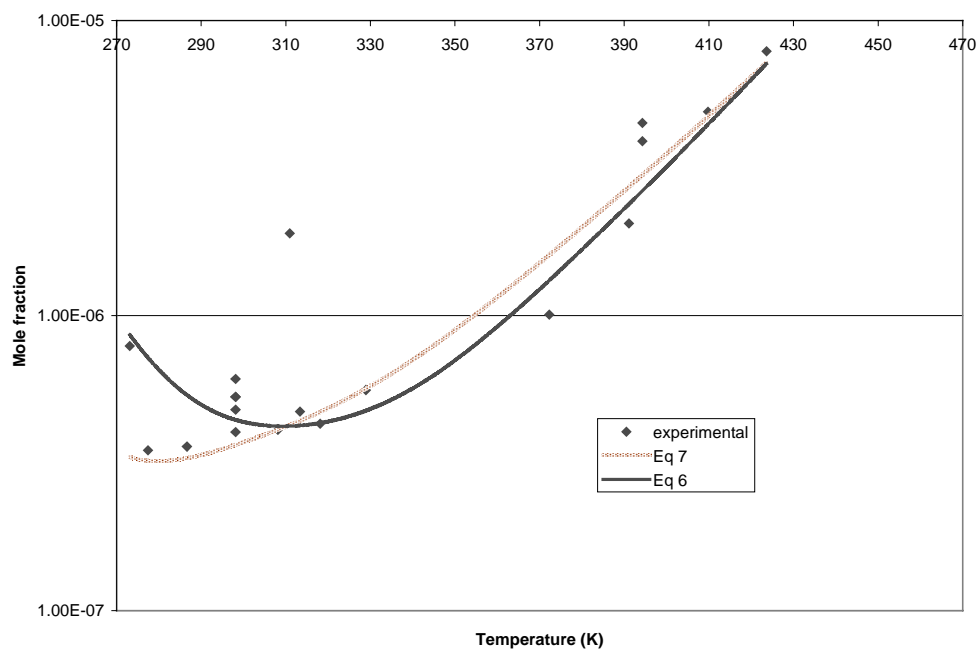


Figure 3: n-Heptane solubility in water as a function of temperature, compared with the values calculated using equations (6) and (7)

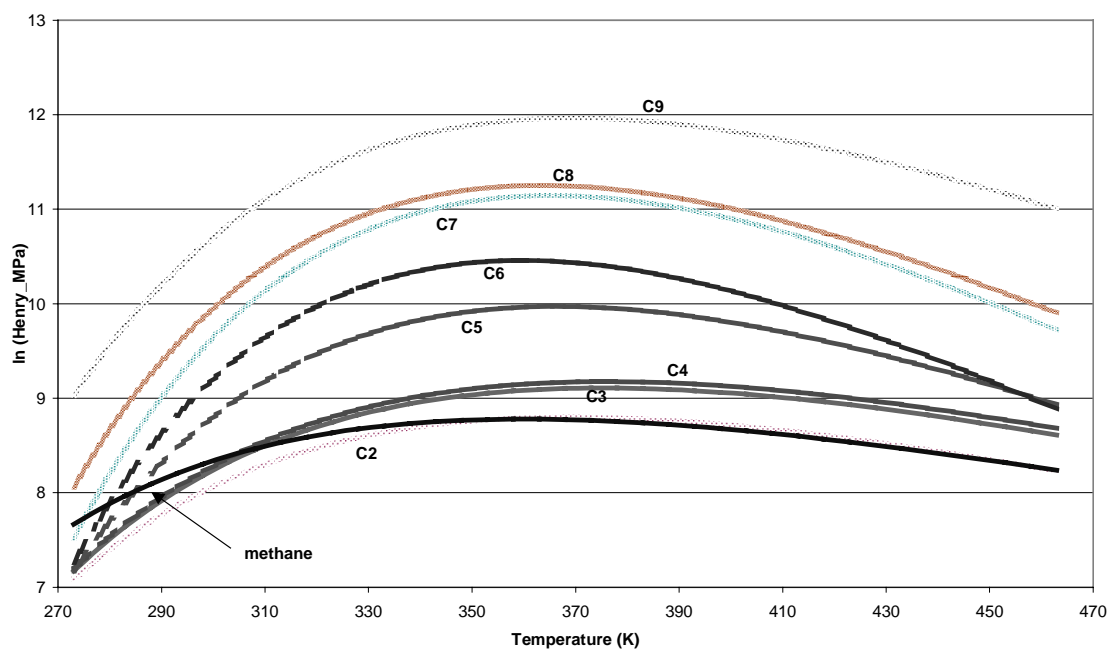


Figure 4: Evolution of the Henry constant for n-alkanes, calculated with expression (6)

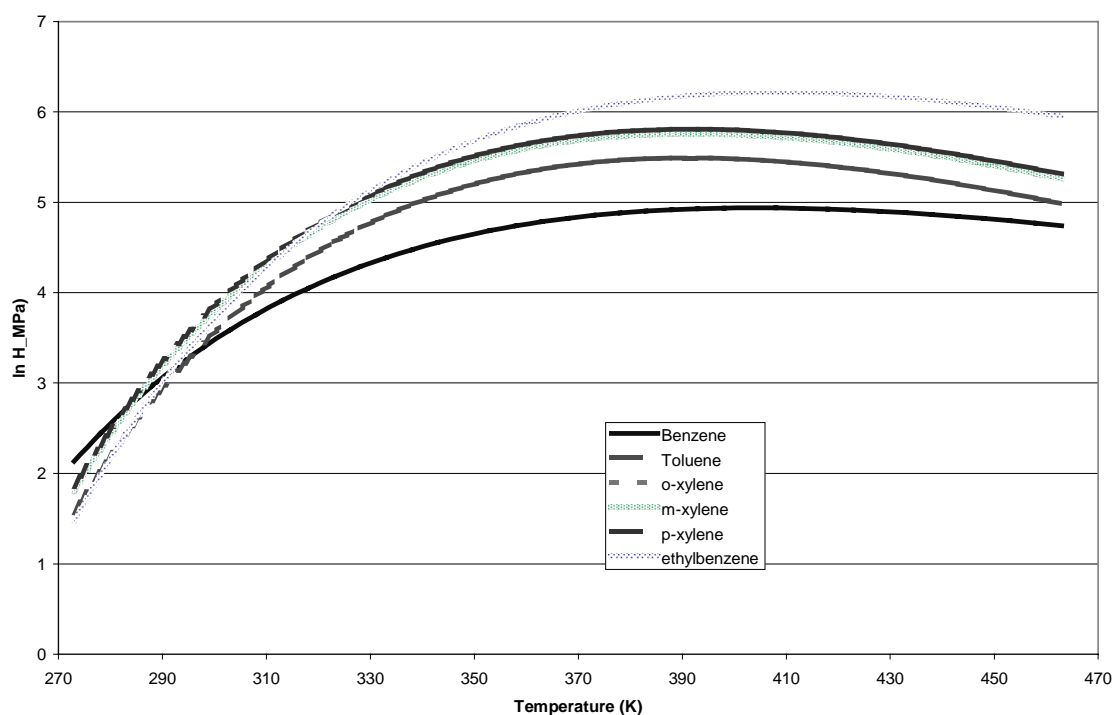


Figure 5: Evolution of the Henry constant for aromatics, calculated with expression (6)

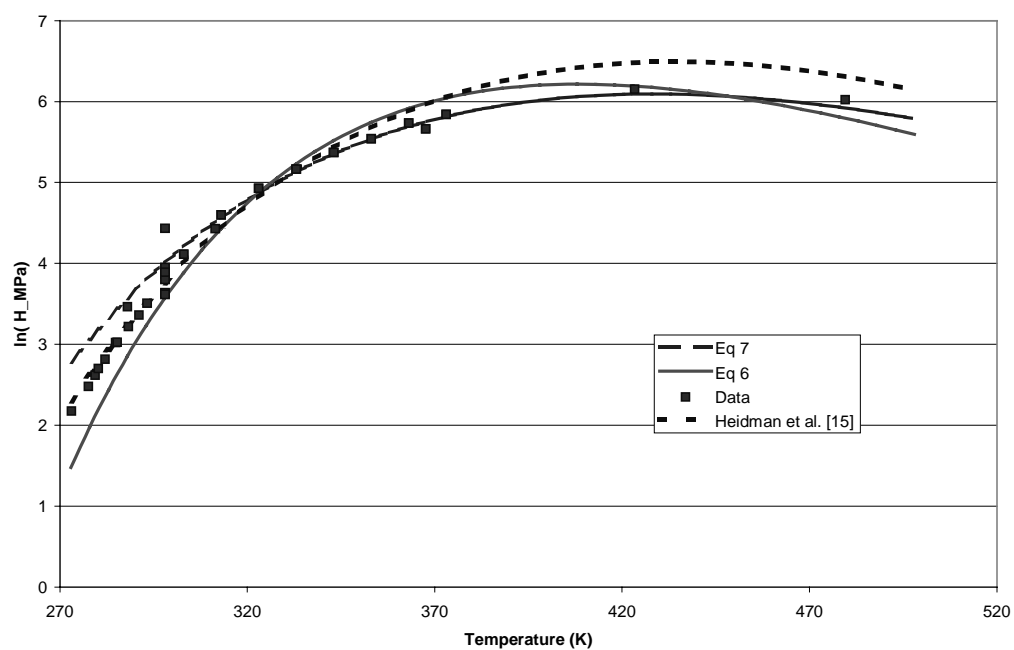


Figure 6 : The Henry constant for Ethylbenzene, as calculated using equation (6), equation (7) and as calculated by the equation of Heidman [15]